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JOURNAL OF

THE INSTITUTE OF PETROLEUM

FOUNDED 1913 INCORPORATED 1914

Vol. 29 APRIL 1943 No. 232

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Published by the Institute of Petroleum.
Address: c/o The Imperial College of Science and Technology, South Kensington, London, S.W.7.
Printed in Great Britain by Richard Clay and Company, Ltd., Bungay, Suffolk.

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Vol. 29. No. 232. April 1943.

VISCOSITY MEASUREMENT AND VISCOSITY INDEX.

By J. C. Cragg, B.Sc., A.I.C., and E. A. Evans (Member of Council).

The assessment of the viscosity temperature characteristics of petroleum products in terms of viscosity index is gaining in popularity. Its recent appearance in Government specifications alone makes its estimation a matter of considerable importance to the petroleum industry. It becomes necessary, therefore, to see clearly how accurately viscosity can be determined, and what effect errors have on the calculated viscosity index. The recent publication of the fourth edition of "Standard Methods for Testing Petroleum and its Products" contains a recommended method for the measurement of viscosity in absolute units, and a considered statement that the apparatus should measure viscosity with an error not exceeding 0·3 per cent. The adoption of this method, with its implied reproducibility, introduces such a change, that a review may be of assistance to those whose acquaintance with it may not be close. To impose a standard of accuracy is laudable, if it can be attained with reasonable skill and equipment. The petroleum industry in America has had experience with a similar method,[2] and believes that it can reasonably maintain an even greater precision than that imposed by the Institute of Petroleum. It will be interesting to observe the agreement forthcoming between workers in this country and the U.S.A. when they measure the viscosity and viscosity index of identical petroleum oils.

Viscosity index[3] is an empirical number and is calculated from the equation:

$$\text{V.I.} = \frac{L - U}{L - H} \times 100$$

where

U = viscosity at 100° F. of the oil under examination;
L = viscosity at 100° F. of an oil of V.I. = 0 (selected Texas Coastal type);
H = viscosity at 100° F. of an oil of V.I. = 100 (selected Penna type);

all three oils having the same viscosity at 210° F. The calculation of viscosity index was originally based upon Saybolt units.[4] Consequently if the accuracy obtainable with the Saybolt viscometer is insufficient, and this instrument is abandoned and replaced by another instrument of greater precision, viscosity index must be based either on other units or on conversions to Saybolt units. The system based on kinematic units[5] is now generally accepted as being superior to Saybolt seconds.

Before proceeding, it is convenient to know the numerical deviations in viscosity index created by errors in viscosity determinations. Table I shows the possible deviation from the mean in V.I. units for a specified viscosity error.

TABLE I.

Viscosity at 210° F., centistokes.	Possible deviation from mean in V.I. units for stated viscosity error.							
	0·25%.		0·5%.		1%.		2%.	
	V.I. 0.	V.I. 100.	V.I. 0.	V.I. 100.	V.I. 0.	V.I. 100.	V.I. 0.	V.I. 100.
2·0	3	3	6	5	12	9	24	18
4·0	3	2	6	4	12	7	23	13
6·0	2	1	4	3	8	5	16	9
8·0	2	1	4	2	7	3	13	7
12·0	2	1	3	1	6	3	11	5
20·0	1	1	2	1	5	2	10	4

As the theme of the paper is founded upon this conception, its meaning should be made clear by means of a diagram (Fig. 1).

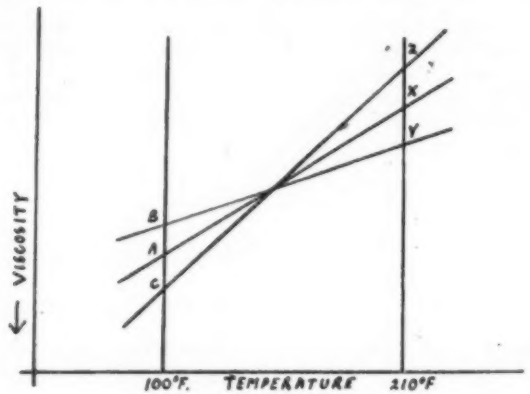

FIG. 1.

AB AC, *XY*, and *XZ* represent stated viscosity error (*x* per cent.).
AX represents the viscosity characteristics giving the true or mean V.I.
BY represents the viscosity characteristics giving the maximum V.I. obtainable with an error of *x* per cent.
CZ represents the viscosity characteristics giving the minimum V.I. obtainable with an error of *x* per cent.

In this country Redwood viscosity [6] is accepted in most trading transactions. The weaknesses of Redwood viscometers have been discovered, and much time and thought have been expended upon improvement. Finally it was agreed to accept Redwood viscometer No. 1307 as the standard. The reproducibility obtainable with N.P.L. certified No. 1 Redwood viscometers is stated by the I.P.[6] to be 1 per cent. of the mean value for efflux times of over 100 seconds at a temperature not exceeding 140° F., while at a temperature of 200° F., and also for viscosities lower than 100

seconds, the viscosity should not differ from the mean value by more than one second. This precision is sufficiently good for works control, has been satisfactory for trading, and is within the requirements demanded by efficient lubrication. Moreover the instrument is convenient to manipulate. Since recognized tables do not exist for the calculation of V.I. from Redwood seconds, it is necessary to convert to kinematic units, in order to calculate V.I.

The conversion of Redwood seconds to kinematic units was first investigated by Higgins,[7] who, in 1913 put forward the formula :

$$\nu = AT - B/T$$

where

$$A = 0{\cdot}00260$$
$$B = 1{\cdot}715$$

and

$$T = \text{Redwood time.}$$

Later Barr [8] pointed out that if Higgins had ignored one abnormal result he would have deduced a value for A of 0·00255, and so sailed nearer the truth. Garner and Kelly [9] tabulated other proposed values for A and B and advanced evidence to show that a single conversion equation was inadequate. Barr [10] returned to the subject, and showed that at a temperature of 70° F. the relationship between Redwood seconds and kinematic viscosity could be represented by two equations of the same form, evaluating ν/T in centistokes per second.

$$\frac{\nu}{T} = A - \frac{B}{T^2}$$

where

$A = 0{\cdot}264$, $B = 189$ when T is less than 91 seconds ;

and

$A = 0{\cdot}247$, $B = 50$ when T is greater than 91 seconds.

Garner, Broom, and Taylor [11] made the very valuable contribution that the relationship at the usual temperatures of 70° F., 140° F., and 200° F. can be expressed by equations of the general type :

$$\nu = \frac{T}{10} \times k^{(1 - A/T^2)}$$

This type of equation [12] had previously been proposed for conversion of Saybolt seconds into kinematic units. In 1936 the I.P.T. published its Viscosity Nomogram [13] based on these results. It gave the first authoritative relationship between Redwood seconds and kinematic viscosity with a probable accuracy of 0·5 per cent.

Using this Nomogram the maximum errors that should occur in arriving at kinematic viscosity by means of an N.P.L. certified No. 1 Redwood instrument may therefore be ±1·5 per cent. at 100° F., and ±2·5 per cent. at 210° F. when the efflux time is about 50 seconds, but if the time is about 100 seconds, the error at this temperature would be reduced to ±1·5 per cent. For the calculation of viscosity index such errors would cause too much deviation. Even assuming that the probable error is two-thirds of the

maximum error, considerable deviations would still be possible. It should be acknowledged that large errors in V.I. are less likely to occur if the same N.P.L. certified Redwood instrument is used for determining the viscosities at both temperatures.

From these considerations it appears that the Redwood viscometer does not give the requisite degree of accuracy for the calculation of V.I., except perhaps for oils of relatively high viscosity.

An effort was made in 1923 by the British Standards Institution to replace the Redwood viscometer by U-tube viscometers, through the publication of a British Standard Specification. A second edition was published in 1929 and a third in 1937,[14] so there had been ample opportunity for study and criticism of the design and method. The precision of the method as a whole is not clearly stated by the standardizing authority, but the effect of various errors on the time of flow of liquids in individual viscometers is discussed. An attempt has been made below to summarize and assess these errors.

1. *Dimensions.*—These are such that within the degree of accuracy (0·5 per cent.) and above the minimum viscosity for which the instrument is designed, the time of flow of a liquid will be proportional to its kinematic viscosity. Using the approximate corrections for kinetic energy provided, no error due to this cause should exceed 0·1 per cent.

2. *Filling.*—Provided that the viscometer is filled to within 0·2 mm. of the appropriate mark on the wide tube, no error exceeding 0·5 per cent. should occur. If liquids which have the same surface tension are compared (such as petroleum products), then the filling error should not cause an error of more than $\pm$0·1 per cent.

3. *Deviation from the Vertical.*—The capillary of the viscometer should be within 1 degree of the vertical in any plane. The error in time of flow due to a deviation of 1 degree should not exceed $\pm$0·2 per cent.

4. *Temperature Control.*—This should be such that three estimations of the time of flow do not differ by more than 1 per cent. If the mean of these readings is taken, this error should not exceed $\pm$0·3 per cent. This does not take into account any inaccuracy in the thermometer.

5. *Timing.*—The stop-watch should be reliable, reading to one-fifth of a second; it should be checked frequently, and should be fully wound before use. No error is indicated by the specifications for timing. For the type of stop-watch indicated an error of $\pm$0·15 per cent. may be considered reasonable.

6. *Calibration.*—This is carried out using one or more of three standards: distilled water, 40 per cent. sucrose solution, and 60 per cent. sucrose solution, depending on the size of the viscometer to be calibrated. "Stepping up" is allowed. The constant obtained is considered to be independent of temperature, as it increases by less than 0·1 per cent. between 0° and 100° C. No indication is given of the probable accuracy of this constant.

From these considerations, and assuming no error in the calibration constants of the viscometers, it should be possible to measure viscosity by this standardized method with a maximum error of $\pm$0·85 per cent. Even if a probable error of $\pm$0·55 per cent. is assumed, the effect on the estimation of V.I. is considerable, as shown in Table I.

Many operators have found that differences are encountered when

determining the kinematic viscosity of the same oil in different B.S.S. viscometers, all of which have been calibrated by the N.P.L. As these discrepancies occur in purely comparative work, in which many of the errors assessed above can be practically eliminated, further thought must be given to the subject. The phenomena are particularly noticeable when determining viscosity with a No. 2 B.S.S. viscometer which has been calibrated with 40 per cent. sucrose solution and with a No. 3 B.S.S. viscometer calibrated with 60 per cent. sucrose solution. Steiner,[15] working with four B.S.S. viscometers, the constants of which had been determined by the N.P.L., found the variations shown in Table II. He thus found an overall difference

TABLE II.

B.S.S. Viscometer No.	Difference, per cent.
2	+0·52
3a	0·00
3b	+0·24
3c	−0·21

of 0·73 per cent. Another worker arrived at a figure of 0·6 per cent. when working with B.S.S. viscometers at his disposal.

When the viscosity of an oil was estimated by us in a No. 2 and in a No. 3 B.S.S. viscometer simultaneously, at the same temperature, a better correlation was found. These results are shown in Table III.

TABLE III.

B.S.S. Viscometer No.	Filling No.	Time of flow, seconds.	C (by N.P.L.).	Viscosity, centistokes.
3(d)	1	195·5		
		195·4		
		195·6		
	2	195·5		
		195·4		
		195·6		
		average		
		195·5	0·3420	66·82
2(b)	3	1406·2		
		1406·6		
		1406·4		
	4	1407·0		
		1406·0		
		1406·2		
		average		
		1406·4	0·04768	67·06

Difference 0·36 per cent.

Barr [10] had previously shown that the calibration constant of a particular No. 3 tube derived from observations with 60 per cent. sucrose agreed within 0·3 per cent. with the constants deduced by means of (*a*) oils whose absolute viscosity had been measured in a capillary tube viscometer of accurately known dimensions, (*b*) stepping up from No. 1 via No. 2 using Bingham's value for water, (*c*) stepping down from the viscosity of a syrup-

glycerol mixture determined by the falling-sphere method. Unfortunately Barr has not given any comparative figures obtained by the use of 40 per cent. sucrose.

Steiner [15] has shown also that the calibration constant of an individual viscometer may vary with the time of flow, but he does not claim that this is common to all B.S.S. viscometers. For his standard he selected a No. 3 B.S.S. viscometer whose calibration constant was reliable throughout its range when compared with a viscometer of different design. For the information of the authors he compared his standard with their standard No. 3 B.S.S. viscometer, which was N.P.L. certified, and found that in some parts of their range the " calibration constant " of the authors' viscometer varied by 0·3 per cent. From these investigations the following may be deduced :—

1. The use of calibration constants derived from 60 per cent. sucrose solution may result in differences in viscosity of 0·3 per cent.
2. Calibration constants based on 60 per cent. and 40 per cent. sucrose solution respectively sometimes vary by 0·7 per cent.
3. Calibration constants may vary within the range of the instrument.
4. An appreciable discrepancy may exist between a No. 1 and a No. 2 B.S.S. viscometer if the calibrations are made with water and 40 per cent. sucrose respectively.

In Table IV are the results,[16] published in 1938, of the viscosity determinations on the same oil by five different laboratories of the highest integrity

TABLE IV.

N.P.L.	Britain	20·98 cp
P.T.R.	Germany	20·54
B.S.	U.S.A.	21·00
E.N.S.P.	France	21·63
B.P.M.	Holland	20·98

and skill. From the status of these laboratories it is safe to assume that they would select the method in which they had the utmost faith. The maximum difference between these results is 5·3 per cent. The inference to be drawn is that there is a definite need for international standardization. This was actually attempted by calling a meeting of the International Standards Association's Sub-Committee on the Viscosity of Petroleum Products in January, 1939, but no results were obtained from that meeting, owing to the war. Between the British, American, and Dutch laboratories there is a difference of only 0·09 per cent. Whether these three laboratories all used B.S.S. viscometers is not recorded in the published records, but the commendable closeness of the results suggests that instruments of the same basic type were used. The German laboratory may have used the suspended-level viscometer, and the French the Vogel-Ossag. The primary standard employed as the basis for the measurements is not recorded, but had all the laboratories taken values for water ranging from 1·0064 to 1·007 centistokes at 20° C. there would be insufficient variation to account

for the differences shown in the results. If these assumptions are correct, it follows that at least two of the viscometers were subject to errors that had not been correctly assessed.

Consideration may now be given to Table V, which shows some results on the same seven samples of oil, obtained in 1941 by four reputable laboratories in the U.S.A. while investigating the relationship between kinematic viscosity and Saybolt Furol viscosity for the A.S.T.M.[17]

The type of viscometer used is not stated, but it is reasonable to expect that it was of the Fenske or suspended-level variety, since at that time the A.S.T.M. was virtually committed to these two types.

TABLE V.

Sample.	Kinematic viscosity at 122° F.				Maximum difference, per cent.
	1.	2.	3.	8.	
A . .	662·0	660·9	657·4	654·7	1·11
B . .	414·5	415·7	413·5	411·7	0·97
C . .	225·0	225·2	224·6	223·5	0·76
D . .	145·0	145·0	145·0	143·6	0·97
E . .	93·8	93·9	93·3	93·4	0·64
F . .	64·5	64·6	64·1	64·1	0·78
G . .	47·7	47·7	47·6	47·4	0·63

Both the Fenske and the suspended-level viscometers have been very fully described in the literature. It is perhaps sufficient to indicate their main points of interest, so that comparison may be made with the B.S.S. instruments. Suspended-level viscometers obviate any error due to filling, since the effective head of liquid depends only on the height of the liquid from a point in the suspended level, and does not depend at all on the height of the liquid in the other limb of the viscometer. Any error due to misalignment is reduced by placing the suspended level directly under the upper bulb. This type of viscometer avoids any bottom-bulb errors, but, on the other hand, top-bulb errors are not compensated in the lower bulb. In the suspended-level types with spherical shoulder, differences due to surface tension in the liquids examined are eliminated.

With the Fenske viscometer a definite volume of liquid between fixed temperature limits is charged to the instrument, so that the same weight of liquid is used for viscosity determinations on the same sample at different temperatures. This procedure necessitates the use of different calibration constants for the different operating temperatures, and has the disadvantage that once the instrument is charged, the operator cannot check the volume of liquid. The error due to misalignment is reduced by placing the upper bulbs directly over the lower, which is made comparatively large to reduce errors due to incomplete drainage.

It is stated in the A.S.T.M. tentative method [2] that any viscometer employed shall be capable of measuring viscosity with an error not greater than $\pm 0{\cdot}2$ per cent. within its viscosity range. How, then, can this statement be correlated with the maximum differences in viscosity shown in Table V? The explanation, at least in part, may lie in the method used for calibrating the viscometers. Except in the case of the suspended-

level viscometers with capillaries less than 0·75 mm. in diameter, the calibration of which is based on the primary standard pure distilled water, all calibrations are based on oil samples. These oil samples are secondary standards, and may be obtained from the A.P.I. or the Bureau of Standards. The determination of the viscosity of an unknown oil therefore depends not on a single viscosity measurement, but on three separate and distinct operations—namely, the determination of the viscosity of the secondary standard by the standardizing authority, the calibration of a viscometer using the secondary standard, and the determination of the viscosity of the unknown oil using this calibrated viscometer. If it is assumed that standard oil from the same bulk is supplied to two laboratories, it is possible for their results on a given unknown sample to differ by as much as 0·8 per cent., although no error greater than $\pm 0{\cdot}2$ per cent. has been made on any single viscosity determination. Any difference that may exist between secondary standards, due to storage or errors in determining the viscosity by the standardizing authority, and any wandering of the calibration constant of a particular viscometer will, of course, further influence the results. The average difference of 0·83 per cent. given in Table V may be said to be quite reasonable and very close to the expected probable error. It may also be inferred that $\pm 0{\cdot}2$ per cent. is sufficient margin to cover errors due to temperature, temperature control, timing, alignment, and filling, but is insufficient to cover errors due to calibration with which must be associated errors due to kinetic energy, surface tension, and any idiosyncrasies of a particular viscometer that may cause the calibration constant to vary with the time of flow or temperature.

These recent A.S.T.M. methods are of immediate interest, because it is upon them that the Institute of Petroleum has based its new standard method for determining viscosity in kinematic units.[1] The I.P. methods are, in general, more detailed than the A.S.T.M., and specify the B.S.S. viscometer in addition to the Fenske and supended-level types with spherical shoulder. The square-shouldered suspended-level viscometer is not allowed. Efforts have been made to minimize some errors. Suitable time-recording devices are described in detail, and thermometers graduated to 0·05° F. are specified as against 0·1° allowed by the A.S.T.M. In addition, the minimum flow time for calibration and referee work is set at 200 seconds, compared with the A.S.T.M. figure of 150 seconds, while for routine work the lower limit is 120 seconds, as opposed to 80 seconds. Suitable constant-temperature baths are described, together with details of the electrical apparatus to employ, but rigid adherence to these details is not called for, possibly because more advanced methods are available. With these advantages of refinement the I.P. state that the apparatus should be capable of measuring viscosity with an error not greater than $\pm 0{\cdot}3$ per cent., compared with the A.S.T.M. figure of $\pm 0{\cdot}2$ per cent.

The possible error due to calibration of all the various types of viscometers has not been considered in the I.P. Method of Test, hence a few comments on this important aspect are clearly indicated. For suspended-level viscometers pure distilled water is the primary standard, the viscosity being taken as:

1·0068 centistokes at 68° F.
0·689 centistokes at 100° F.

This standard is directly applicable only to No. 1 viscometers of this type. For B.S.S. viscometers the primary standards are pure distilled water, 40 per cent. sucrose solution, and 60 per cent. sucrose solution, although an observation is made that the figures for the 40 per cent. sucrose solution may require revision. For Fenske viscometers, and also for both the other types, the use of secondary oil standards, as issued by the A.P.I. and the Bureau of Standards, is allowed, in addition to oil samples the viscosity of which have been determined by the N.P.L. The calibration constant determined at 100° F. is considered valid for all other temperatures in

TABLE VI.

Oil.	Filling.	B.S.I. tube No.	Temperature.	Time of flow, seconds.	Viscosity, centistokes.
A.P.I. Beta 42	1	2(b)	210° F.	507·0	
				507·0	
				507·0	
	2			506·6	
				507·4	
				507·0	
				average	
				507·0	24·17
A.P.I. Beta 42	3	3(f)	100° F.	1124·0	
				1122·0	
				1123·0	
				average	
				1123·0	384·0
A.P.I. Alpha 42	1	3(f)	100° F.	182·2 *	
				182·0	
				182·0	
	2			181·8	
				182·0	
				average	
				182·0	62·20

* Flow time rather low for calibration purposes.

the case of the suspended-level types, whilst factors are given to evaluate the calibration constant at various other temperatures in the case of the Fenske.

The order of reproducibility that can be achieved using B.S.S. viscometers calibrated by the N.P.L. with sucrose solution has already been discussed. Table V gives an indication of the reproducibility that may be expected when working with viscometers calibrated from A.P.I. or Bureau of Standards secondary oil standards, while Table VI shows some results obtained by the authors when measuring the viscosity of secondary oil standards in B.S.S. viscometers whose calibration constants have been reported by the N.P.L. Table VII shows the recorded A.P.I. figures and the differences from our own.

The agreement using the No. 3 B.S.S. viscometer is quite good, being well inside the error inherent from its calibration with 60 per cent. sucrose solution. The results obtained at 210° F. using the No. 2 B.S.S. viscometer

are disturbing. They may be due to a combination of factors, although the greatest error can probably be associated with the published data on the 40 per cent. sucrose solution used in the calibration of the No. 2 B.S.S. viscometer.

It may be said with some confidence that the large number of standards now allowed by the I.P. do not give consistent results among themselves, and a discrepancy of anything up to 1 per cent. in the estimation of kinematic viscosity must be expected between two operators when the particular standard to use had not been clearly specified. In lubrication this is usually of minor consequence, but when the calculation of V.I. is involved the discrepancies assume greater significance. It is perhaps fortunate that the accurate determination of viscosity index does not require the true

TABLE VII.

Oil.	Temperature.	A.P.I. recorded viscosity figure, centistokes.	Difference, per cent.
A.P.I. Beta 42 . . .	210° F.	23·91	1·09
A.P.I. Beta 42 . . .	100° F.	384·0	nil
A.P.I. Alpha 42 . . .	100° F.	62·33	0·20

viscosity with a high degree of accuracy. It is sufficient for the purpose of V.I. that viscometers should measure viscosity accurately against an arbitrary standard. For convenience this may coincide with one of the recognized standards, at some definite temperature and for some definite flow time. It must be borne in mind that when the viscosity of a petroleum product is measured at two temperatures to determine the V.I., two viscometers of differing ranges are usually employed. It follows that the calibration constant of these two instruments should be based on the same standard, whether it be 40 per cent. or 60 per cent. sucrose solution, pure distilled water, or one of the secondary standards. It is also advisable to use viscometers of the same basic type, and not a combination of different types of viscometers, some calibrated against one standard and some against another. Steiner [15] suggests the procedure of selecting a viscometer whose calibration constant is probably reliable within the whole range of the instrument, and regarding this instrument as the laboratory standard, at least for V.I. considerations. Other viscometers with the required viscosity range are then carefully compared with the selected viscometer throughout their entire range, and the calibration constants for various flow times are determined. The calibrating procedure would involve much precision work. If this is carefully done the " constants " should be reliable to $\pm 0{\cdot}1$ per cent. When these viscometers are used with all the other refinements of the new I.P. method, it should be possible to measure viscosity against the arbitrary standard with a probable error of $\pm 0{\cdot}25$ per cent., which is adequate for the calculation of V.I.

The use of charts, or the equations on which they are based, has not been considered in this paper, as it is obvious that they introduce other errors into the calculation of V.I. Apart from the usual charting errors, it is

realized that the very ingenious and useful formulæ which have been suggested are designed to fit experimental results. Such methods, then, are not to be recommended for determining viscosity from which V.I. is to be calculated.

In the U.S.A. there has been an opportunity to obtain experience with the newer methods for determining kinematic viscosity and their application to the calculation of V.I. In this country we are on the threshold of obtaining such experience. Until the sellers and the buyers of oils have thoroughly understood the difficulties, there may be misunderstandings. It is prudent, therefore, to abstain from overstating the accuracy of these methods, and to content ourselves with the conviction that they are superior to those which are being dislodged.

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[16] Second Report on Viscosity and Plasticity, 1938. Prepared by the Committee for the Study of Viscosity of the Academy of Sciences at Amsterdam.
[17] A.S.T.M. Standards on Petroleum Products and Lubricants, 1941, 2 pp.

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THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute of Petroleum was held at the Junior Institution of Engineers, 39 Victoria Street, London, S.W.1, on Friday, 29th January, 1943, at 4 p.m. In the absence of the PRESIDENT, the Chair was occupied by Dr. F. H. Garner.

The following paper was read by Mr. J. C. Cragg :—

"Viscosity Measurement and Viscosity Index." By J. C. Cragg, B.Sc., A.I.C., and E. A. Evans (Member of Council) (see pp. 99–109).

DISCUSSION.

THE CHAIRMAN said that the paper was a very interesting one and should serve as a valuable focus for discussion on the question of the accuracy of viscosity measurements.

Before the discussion began it would be interesting to consider the way in which the requirements of accuracy were stated in the I.P. standard method, first with regard to scope, and then with regard to the apparatus. The statement under the latter head was as follows : "The apparatus shall be of the capillary type, and shall be capable, with proper manipulation, of measuring viscosity with an error not greater than 0·3 per cent. within the viscosity range with which it is to be used"; in other words, the figure might be either 0·3 per cent. over or 0·3 per cent. under the true viscosity, and he thought that was on the high side. The error in the procedure was again to be not more than 0·3 per cent. Therefore, if one happened to have an instrument which was 0·3 per cent. out, it was possible to have an additional error of 0·3 per cent., so that the result obtained could be 0·6 per cent. too high or 0·6 per cent. too low, a maximum error of 1·2 per cent., as compared with the A.S.T.M. figure of 0·8 per cent. However, it was the probable error that should really be considered rather than the maximum error, and it could be assumed that the probable error would be about half the maximum error, so that the viscosity determined according to the I.P. standard method should be within 0·3 per cent. of the true viscosity.

With regard to Table V, Sample A, which had the highest viscosity, had a Saybolt Furol viscosity of 310, so that it was possible that that oil was not a lubricating oil, but a fuel oil of the Bunker C type; the deviation in the kinematic viscosity was twice the deviation in the Saybolt Furol viscosity, which was rather unusual, so perhaps it was justifiable to leave Sample A out of consideration.

Another point was that the Kinematic Viscosity of laboratory No. 8 was low compared with the other figures. If these values were omitted, the accuracy would be very considerably improved.

Mr. Cragg had referred to the work of the International Standards Association. That work had involved the use of a series of U-tube viscometers calibrated by the N.P.L., which were circulated to all the standardizing authorities. The times of those tubes were first determined by the N.P.L. on two oils; then the viscometers were sent out to the various countries, with three other oils, and the times were run together with the kinematic viscosities determined by the standard method in use in the particular country concerned. The results, unfortunately, had not been completed, owing to the war, but a number of results had been obtained, which Dr. Barr sent to him last week, and he proposed to put them on the blackboard at a later stage of the meeting.

PROFESSOR GARNER subsequently wrote :—

The point has been made in the paper that the accuracy required in viscosity determination for actual lubricating-oil requirements is much less than that specified in Standard Methods of Test but the accuracy limits in viscosity determinations are determined by specification requirements. It is generally agreed that the figures

quoted in specifications should be taken as absolute—that is, that it is not permissible to include experimental errors and therefore if the viscosity requirements specify figure A and the experimental error is B, then the viscosity which actually has to be met is $A + B$ or $A - B$, depending on whether A is a maximum or minimum viscosity. Where there is no great difficulty from the supply point of view in meeting the viscosity requirement, very great accuracy is not required in laboratory determinations, and thus the figure B can be made much larger than is specified in the Institute of Petroleum Standard Method, still making sure that the absolute requirement of the specification—namely, A—is met. On the other hand, in the case of high-viscosity-index oils, it may be desirable and necessary for the supplier to have available viscosity methods and apparatus which enable him to meet the specification requirements with the minimum of error, and for this purpose B should be as low as possible—for example, as specified in the A.S.T.M. procedure, $\pm 0{\cdot}2$ per cent.

The second point concerns the accuracy of the Redwood Viscometer. The Institute of Petroleum Standardization Sub-committee dealing with the Redwood Viscometer some years ago spent much time trying to improve the possible accuracy of the instrument, as, for example, by increasing the accuracy with which the orifice tube is drilled, and it considered for this purpose the use of stainless steel. A Redwood instrument as an absolute viscometer has two fundamental faults: (1) A shortness of the capillary tube and the difficulty of manufacture with reasonably fine accuracy; and (2) the fact that the jet is not maintained and cannot be maintained at the temperature of test, since the bottom plate of the part of the viscometer bath containing the oil is exposed to the atmospheric temperature.

Thus, as laid down in the Standard Methods of Test, it is not advisable to use times in the Redwood viscometer for conversion to centistokes, as the accuracy expected in centistokes by the I.P. method is greater than that which can be obtained with the Redwood instrument.

Dr. G. Barr, referring to the early history of the U-tube viscometers, said that when he first had some viscosities to measure, all that he could buy in the way of U-tube viscometers from the laboratory furnishers was an Ostwald viscometer, and he had no idea what the capillary would be, the time of flow, or anything else. He looked at a number of different types and patterns of viscometers that had been got out, and it appeared that the type which had now been adopted by the British Standards Institution offered conveniences, in that one did not need a pipette for filling it and did not have to weigh it when it was filled. He had calibrated a series of those tubes, as Mr. Cragg had pointed out, by comparison with an absolute viscometer of which the capillaries had been measured fairly carefully, by comparison with the then accepted value for water and by stepping down, assuming Stokes' law, from the viscosity of a certain viscous syrup of about 80 poises. (In those days poises were used, and not stokes.) When he had completed the calibration he had compared the figure with that given by Bingham for a 60 per cent. solution of sugar of extraordinarily high purity. He himself had not got any of this grade, so he used A.R. sugar. He worked out a curve or formula expressing Bingham's results, and assumed that he could calculate the viscosity of an approximately 60 per cent. sugar solution from the density. That formula was subsequently adopted in the first B.S.I. specification, and he might remark that, over the range in which he had used it, which he thought covered most of the range which was given in the specification, and with all the different brands or types of sugar which he had used, he had always obtained concordance within about 0·3 per cent. At that time 0·3 per cent. was considered extremely good. The only time he got a 60 per cent. sugar solution which did not agree was when he had some super-pure sugar, which he eventually discovered had a rather strong smell of alcohol. As Mr. Cragg had remarked, he did not then check so exhaustively the viscosity of a 40 per cent. sugar solution, and he had not done so since. Having regard to the difficulty of preparing and measuring a solution of 60 per cent. and measuring its viscosity without picking up water, he thought at the time that if he could repeat the 60 per cent. sugar solution, the 40 per cent. sugar solution must be right, and he left it at that, and the value based on Bingham's results was incorporated as a standard for the calibration of No. 2 viscometers in the B.S.I. tubes. Since then he had reason to believe that that standard differed by $\frac{1}{2}$ per cent. or so (sometimes it was 0 and sometimes it was 1) from the standard obtained with 60 per cent. sugar,

and of recent years, when asked to calibrate a viscometer or to determine the viscosity of an oil, he had always taken great care to state in his report whether it depended on a viscosity of 60 per cent. or a viscosity of 40 per cent. It was obvious that for the viscosity index determinations one must have only one of the two. He did not think it mattered very much which it was, but, since the 60 per cent. sugar solution had to be used for the higher and it agreed with other determinations, if one used a sugar solution at all the 60 per cent. sugar solution was the obvious one to use.

There was a more disturbing fact, to which Dr. Steiner had directed attention, and which had also been brought out in the calibration of the thirty-two viscometers used for the international calibration to which Dr. Garner had referred—viz., that the calibration constant could on occasion vary with the time of flow. From the series of I.P. viscometers to which he had referred he had selected the extreme examples. He had compared an oil which gave 909 seconds in the one that he kept at the Laboratory with the flow of that oil in each of the other viscometers, and he had done the same with another oil of 113 seconds. The worst of the No. 2 viscometers gave a ratio of time of flow of 0·715 for the oil of 909 seconds, and 0·7130—*i.e.*, differing by 2 in 700—for the less viscous oil of 113 seconds. That result was not too bad, especially as the No. 2 viscometer was the one which had been giving most trouble. With the No. 3 viscometers, however, the ratio changed from 0·881 to 0·886 when the time varied from 160 to 480 seconds, so there was the $\frac{1}{2}$ per cent., or a little more, straightaway.

He was not prepared to say what that variation could be due to, but one obvious suggestion was that, when one had filled to the filling mark and the oil had been sucked up into the timing bulb, there was a certain amount of oil left in the lower bulb, the quantity of which might vary with the viscosity of the oil. That was all very well, but what one was concerned with was not that quantity of oil, which it was true would make a difference in the viscosity, but the variations in the quantity of oil between different viscometers, and, if the variation of $\frac{1}{2}$ per cent. or so was to be assigned to the oil which was left behind in the lower bulb, the quantities of the oil left behind must vary between different viscometers, and not only in the same viscometer.

In Table IV the authors had listed the results of some oil determinations of about twenty-one centipoises, and said that whether the three laboratories which agreed—namely, the British, American, and Dutch—used B.S.S. viscometers was not recorded. In that connection he would say that the Bureau of Standards almost invariably used a Bingham type of viscometer, with applied pressure; the British N.P.L. used a B.S.I. instrument, and he was not sure what the Dutch used. He was almost certain that the German laboratory would not have used a suspended-level viscometer, which was due to Ubbelohde, because Dr. Erk had a special absolute viscometer of his own at the Reichsanstalt, and the oil determinations there were presumably based on that absolute viscometer. He might say that Dr. Erk's figures had tended to disagree with those of the other countries in other determinations. A pair of U-tubes had been circulated about 1934 for calibration by different countries, and in that case also the German laboratory was different. With regard to the French determinations, the *Ecole Nationale* used to use a Louis viscometer of an absolute type, and in the comparisons to which he had just referred there was a very serious discrepancy between the French determinations and the remainder.

He had not studied the question of the correct method of assessing possible errors in results if an error of 0·2 per cent. was made in three different connections. It was true that the error might be the sum of all of them, but he thought that in general, as Dr. Garner had remarked, the probable error was not really the whole sum.

Dr. N. Anfilogoff said that in listening to the paper he had been constantly reminded of the story of the student who took the result of a mathematical calculation to his professor, the figure he had arrived at being 0·525643, and the professor looked at the figure and said : " Well, I do not know about the 643, but the 525 is certainly wrong."

He entirely agreed with what the authors had said in the last paragraph of their paper, that there was a tendency to overdo viscosity index, particularly in connection with commercial specifications. He thought it was a kindly warning that the authors had given, lest one day it might be necessary to meet a specification with a minimum V.I. of 64 and a maximum V.I. of 65.

There was one point to which he would like to refer in connection with Table IV. In 1938 he had sent an identical sample to the French naval laboratories at Toulon,

Paris, and Rouen, and to laboratories at Antwerp, Berlin, and Strasburg, and also to the N.P.L., and the difference in viscosity was of the order of 6 or 7 per cent. It was interesting at the time to note that his own laboratories showed a very much smaller difference between themselves than the three standard laboratories, and also that they were closer to the N.P.L. than to any of the Continental laboratories. Their instruments were based on American standard calibration. It was interesting to see that the figure which Dr. Barr had obtained at the N.P.L., and the figure obtained at the Bureau of Standards had only $\frac{1}{10}$ of 1 per cent. difference between them. Dr. Barr's results really corroborated what he had found, that the English figures were very different from those of the French and Germans. He had found exactly the same thing in the sulphur determination of a lubricating oil.

Dr. Broom said he would like first of all to congratulate the authors on their thought-provoking paper, with much of which he was in complete agreement.

When the tendency to use kinematic viscosity grew up among petroleum technologists they probably thought that by abandoning, or partly abandoning, the use of the Redwood viscometer and changing over to kinematic viscosity, they were giving themselves a better tool, which was correct; but perhaps they also assumed that they would obtain better results and do a better job of work just because they were using a better tool, and that, of course, did not follow at all. In general, the U-tube type of viscometer would give better results, but it must be recognized that the same degree of painstaking work was necessary in order to obtain accurate results; in other words, it was necessary to observe all the details about temperature, and so on, just as carefully as with the Redwood instrument. The point was that, if that was done, then a better and more correct result was obtained than with the Redwood viscometer.

With regard to the question of sugar solution, he had tried at different times to calibrate No. 2 B.S.I. U-tube viscometers with 40 per cent. sugar solution, and he had compared the answer with what he obtained when he stepped up from a viscometer suitable for the use of water. He always found a difference in the two methods of approximately $\frac{1}{2}$ per cent. At first he thought that that was probably his fault, that he had made some mistake, but after it had happened more than twice he began to think that there might be something wrong with the 40 per cent. sugar solution, and he believed that had been the experience of several people. Quite apart from the question whether the 40 per cent. sugar solution or the 60 per cent. sugar solution was right or wrong as a basic standard, he had always thought that its use was not a good method to stipulate in a standard methods book, because the tendency would then be to assume that it was a method that could be applied in almost any laboratory and the right answer obtained. Dr. Barr had referred to the difficulties experienced in working with a sugar solution, and they were very considerable, because the solution was hygroscopic, and it was necessary to take fairly elaborate measures to ensure that the particular specimen the density of which was being measured remained the same when in the viscometer and while it was being used. He did not think that was a simple sort of thing for a routine laboratory to do. It might be that a sugar solution could be used satisfactorily in laboratories such as those mentioned in Table IV of the paper; for instance, the N.P.L.

In considering the question of accuracy in general, he had always regarded it as being composed of three parts. Firstly, the question of the basic accuracy came down in the end to an absolute measurement made on a pure chemical liquid, a liquid of defined and reproducible properties, of which pure water was probably the simplest example. Unfortunately it possessed a viscosity which was far too low for most of the purposes in question, and, if a suitable hydrocarbon could be found which had a viscosity more approaching that of a lubricating oil and well-defined properties which could be checked, that would be a considerable help. Would all the various instruments which measured absolute viscosity in the various standardizing laboratories give the same answer when measuring the same liquid? He was referring now to the absolute instrument, not to any instrument calibrated from it. In other words, what was the viscosity of water? Was everyone agreed on the viscosity of water at 20° C.? If not, it would not be possible, as far as he could see, to obtain agreement between the various standardizing laboratories. If there was agreement on that basic standard, the second question was whether the subsidiary instruments, such as the Ubbelohde, the B.S.I., and so on, when they were calibrated or the smallest one in each range was calibrated with water, would still give, over the whole range, correct answers when

more viscous liquids were used. Was the design of each of those viscometers satisfactory, so that they would give the same constants over long times of flow and short ones, due allowance being made for the kinetic energy errors, and so on? There was the third error, which he supposed might be described as an operational error, and that embraced all the experimental details, such as making sure that the temperature was right and that the viscometer was upright in the bath, and all the operational details of a particular determination. Having regard to these three types of error, his own opinion was that, at the present time, it would be optimistic to expect an absolute error in a viscosity determination of less than $\pm\frac{3}{4}$ of 1 per cent., although the operational error was much less, probably $\pm\frac{1}{4}$ per cent.

With regard to the estimation of viscosity index based on viscosity measurements, he thought that the authors really accepted the viscosity index principle and its use generally; he did not get the impression that they were opposed to its use. It should be realized, however, that in the case of the lighter oils the viscosity-index system was certainly not uniform. Consider, for instance, the theoretical highest maximum viscosity index of an oil, when the viscosity did not vary at all, but was the same at 210° F. as at 100° F. The viscosity index could be worked out for oils of different viscosities, and in the case of the thinner oils the figure was very high, being 366 for an oil of 2 cs., but as the viscosity of the oil increased it flattened out at about 150 for an oil of 50 cs. viscosity. That must be an indication that the viscosity-index scale itself was not linear; in other words, an error of 5 viscosity units would not mean the same on any part of the scale.

Mr. J. Cantor, referring to the question of calibration, said it had been shown that in order to obtain results of the desired reproducibility, it was essential to have a single calibrating liquid only. It was necessary to consider which substance had suitable characteristics so that it should be selected as the sole standard. Considering the existent standards first, water had certain disadvantages. First of all it was of low viscosity and it gave an extremely short time of run when it was used for calibrating viscometers. For instance, in the case of the No. 1 Ubbelohde the times of run were about 100 seconds at 20° C. and about 68 seconds at 100° F., which were much too short. Sugar solutions presented difficulties which had already been mentioned. First, they were hygroscopic, and, secondly, it was difficult to measure the density to five decimal places, which was necessary when sugar solutions were used. Furthermore, there was the doubt with regard to the figures for the 40 per cent. sugar solutions. In addition, there was an inherent difficulty about all aqueous media if they were used for calibrating viscometers which were then going to be used for the determination of oil viscosity. For example, the surface tension of water and of sugar solutions was of the order of 75 dynes per centimetre, whereas in the case of oil it was about 30 dynes per centimetre. That led to considerable errors, for which the A.S.T.M. attempts to compensate. In the case of the calibration of the square-shouldered Ubbelohde, the A.S.T.M. determines the constant of the instrument with water and multiplies that constant by 1·0035 in order to get the correct constant for oil-viscosity measurements. In the case of the spherical-shouldered Ubbelohde, the effect of the surface-tension differences was supposed to be eliminated, but there seemed to be some doubt about that. It had been stated by Cannon and Fenske, he believed, that the error in going from water to oil with the usual capillary viscometers was of the order of 0·3 per cent. to 0·5 per cent., and in general it was obviously difficult to assess accurately the necessary correction.

Other liquids had been suggested as primary standards; for example, Steiner had suggested aniline, which had certain advantages. Its surface tension was much nearer to that of oil, being 44 dynes per centimetre, and it had a kinematic viscosity of 4·5 centistokes at 20° C., which gave sufficiently long times of run to diminish considerably the timing errors. Slight oxidation apparently did not affect the viscosity of aniline much, and it seemed to be a promising material.

He would like to suggest another material for consideration, namely, cetane, the diesel-engine standard. Cetane (*n*-hexadecane) had a viscosity of about 4·5 centistokes at 20° C. or 68° F. It had a melting point of 65° F., and the temperature of 68° F. might be too close to that for safety, but the times of run would still be sufficiently long at 77° F. and at 100° F. for the timing errors to be small. Its surface tension was obviously of the correct order. There would be no difficulty in using for the measurement of oil viscosity a viscometer which was calibrated with cetane. It

would be necessary, of course, to establish that the different batches of engine-standard cetane all had the same viscosity or could be converted to the same viscosity by means of a simple treatment. A number of official laboratories would have to determine the viscosity of cetane with extreme accuracy and to agree upon a figure, and then cetane could be used for the standardization of the No. 1 Ubbelohde, the No. 50 Fenske, and the Nos. 0 and 1 U-tube viscometers. The other viscometers in each series could then be calibrated by means of a very careful stepping-up process. All the viscometers would then be based upon a single substance and there should be interconsistency in calibration constants. Possibly some other substance might be found to be more convenient, but cetane appeared to be the only stable hydrocarbon which was available and which had suitable viscosity characteristics.

There was an alternative method of clearing up the calibration difficulty, which was less attractive theoretically—namely, to abolish primary standards altogether and to calibrate viscometers with secondary oil standards only. These should be issued by a single authority, such as the N.P.L. That single authority would measure the viscosity of these oil standards with a single master instrument, or with instruments whose constants had been obtained on the basis of the master. All viscometers in use would then refer back to that master instrument, leading to interconsistency in their calibration constants.

Some such scheme as the above would seem to be necessary to eliminate the existent confusion in the field of viscometer calibration.

Mr. J. Romney, referring to the question of the possible error in viscosity determination, said it was mentioned in the paper that the error due to one degree deviation from the vertical should not exceed $\pm 0{\cdot}2$ per cent. In the case of temperature measurement the temperature might be too high or too low, giving a deviation in either direction, but in the case of deviation from the vertical was not the error in one direction only? Did it seriously matter, for all tubes, whether the tube leaned over in one direction or the other? The error was not a plus or minus figure. It had been worked out that the possible error on the basis of the B.S.I. tubes was the sum of the various errors, and that was 0·85 per cent. It was also suggested that the probable error was likely to be about half that, which was fairly reasonable, but it should be remembered that the errors due to different points might cancel one another out, and therefore, on this basis alone, the probable error became half. Having regard to the fact also that the probable errors due to each point were themselves likely to be 50 per cent. of the possible errors, he thought it was reasonable to assume that the probable error was about one-quarter of the possible total error, *i.e.*, $\pm 0{\cdot}2$ per cent., which was in line with the 0·3 per cent. mentioned in the I.P. Standard Methods for Testing. At the same time it was important to realize that one could not work out possible errors by calculating theoretical errors due to the different points. The possible errors were those which did actually arise. A series of tables was given in the paper showing the results obtained by different laboratories, and it must be remembered that these were laboratories which were examining oils under conditions in which they knew that the results would be published, so that extreme care must have been taken in the determinations, yet the maximum deviations were a good deal larger than would suggest the accuracy which it was claimed that it should be possible to obtain. Therefore under present conditions too much reliance should not be placed on viscosity determinations to within very close limits. The effect on the viscosity index had been mentioned. The viscosity index was undoubtedly a very useful tool, but did the deviations which resulted from viscosity errors matter very seriously? He regarded the viscosity index as giving a general idea of the viscosity temperature curve of an oil, and he did not suppose that two or three points either way, or even five points, mattered very much. Dr. Anfilogoff was anxious about the appearance in specifications of too narrow limits and referred to a maximum V.I. of 65 and a minimum V.I. of 64, but personally he did not think that anyone would specify a maximum V.I.; it would be only a minimum. It was well known that an oil with a V.I. of 70 was a good deal better on the viscosity temperature curve than oils of 35, and the effects of viscosity errors on viscosity index were probably not very important, outside specification work.

The viscosity index was based originally on viscosities at 210° F. and 100° F., and he thought it was rather a pity that the temperature of 210° F. had been adopted; it was not a suitable temperature, because it did not allow of water being used as the bath liquid. He thought it would be very useful if somebody in this country could

find time to draw up a table from which could be calculated the viscosity index from viscosities at 200° F. and 100° F. That should be quite feasible; it would involve a good deal of work, but some public-spirited person might be willing to do it. At the moment the temperature of 210° F. had to be used, and he would be interested to have suggestions of a suitable bath liquid for that temperature. The I.P. book mentioned oil, but that would be rather unpleasant when one had to lift the tube out of the bath. Ethylene glycol had been suggested, and he thought that would be a good deal better, but it was almost impossible to obtain it at the present time. He did not know of any other suitable bath liquid.

It was stated in the paper that the reference oils calibrated by the N.P.L. could be used as secondary standards, but that they must be re-checked periodically, and he would be glad to have some information about the changes which had been found to occur in oils in storage in stoppered bottles kept in the dark. He thought it was unlikely that most laboratories would have their reference standards checked as frequently as was suggested in the I.P. book, and he would like to know what would happen if the time between checkings was rather longer than the time mentioned in the book.

It was rather disturbing to learn that the factor for a particular tube might vary with the different times of run, and he would like to have some information about the idiosyncrasies of tubes that caused these changes. If there was anything that one could actually look for, it would be a good deal simpler than having to obtain the factors against the numerous standards that were suggested in the paper.

Mr. Romney subsequently wrote :

Since commenting at the meeting on the calculation of the probable from a series of possible errors, I have taken the opportunity of looking up this subject and of discussing it with mathematicians more expert than I. It seems that the result depends on the interpretation of the term " possible." It is hardly true to say, in the instance under discussion, that the possible errors are those which will never be exceeded. If it is assumed that a possible error is one which will not be exceeded more than once in five times, then reference to a table of the Probability Integral shows that the probable error of a measurement with a possible error of 0·1 is :

$$\frac{0{\cdot}6745 \times 0{\cdot}1}{1{\cdot}2816}$$

The square of the probable error of a sum of quantities is the sum of the squares of the probable errors of the separate quantities. Hence, for the series of possible errors indicated by the authors, the probable error is :

$$= \pm \sqrt{\left\{\frac{0{\cdot}6745}{1{\cdot}2816}\right\}^2 (0{\cdot}1^2 + 0{\cdot}1^2 + 0{\cdot}2^2 + 0{\cdot}3^2 + 0{\cdot}15^2)} = \pm 0{\cdot}2186 \text{ per cent.}$$

If the possible error is one which is likely to be exceeded only once in ten times, the factor becomes :—

$$\frac{0{\cdot}6745}{1{\cdot}6449}$$

and the probable error works out at $\pm 0{\cdot}1703$ per cent.

Even if the possible errors are those which are as likely to be exceeded as not, the probable error becomes $\pm 0{\cdot}4153$ per cent., which is lower than the $\pm 0{\cdot}55$ per cent. mentioned in the paper, but it is unlikely that the authors intended this interpretation to be placed on the term " possible error."

This would appear to suggest that errors in the calibration constants are mainly responsible for the relatively large differences between the viscosity figures reported by different laboratories on the same oils.

Mr. J. S. Jackson thought that ample evidence had been given in the paper and in the discussion to show that the idea that the true viscosity of an oil could be determined within $\pm 0{\cdot}2$ per cent. as an ordinary routine operation was a pure myth. If it was a pure myth, he thought something should be done about it and the Institute should take the matter up strongly with the A.S.T.M., because their method, whatever it really meant, gave the impression that with the apparatus in question that degree of

accuracy could be obtained in ordinary commercial laboratories. It had been said that five points on the viscosity index did not make a great deal of difference, but that was not the case if one had to supply an oil of 100 viscosity index and happened to produce one that was 95 by mistake. On the other hand, if the specification called for an oil of 100 K.V.I., it was obviously not feasible to make one of 105 for safety.

With regard to the question of the No. 2 B.S.I. viscometer, an effort had been made to get out of the difficulty by saying that "it is recognized that the figures for the 40 per cent. sucrose solution may require revision." Dr. Barr had also admitted that he had reason to believe that the 40 per cent. sucrose figures might not be very accurate. Personally he submitted that the average man in the average laboratory up and down England was probably not in a position to appreciate this very unfortunate state of affairs, and if he bought a No. 2 N.P.L. certified B.S.I. viscometer, he would naturally expect it to enable him to determine accurately the viscosity of an oil. If, however, it gave him a figure which differed by about 1 per cent. from the result obtained with a No. 3, he might get into serious commercial difficulties. Therefore he would suggest that the Institute should take the matter up with the B.S.I. or the N.P.L., and in the meantime it was suggested that all reference to the B.S.I. viscometers should be deleted from the Institute's Method Book.

Mr. E. A. Evans said that Mr. Jackson had made remarks that he had intended to make. The Chairman had suggested that there was a legal mind behind the paper, and that there had been a good deal of care exercised in the wording of it. Mr. Marlow, who was known to many of the members, gave a series of lectures on Law which he had attended. In those lectures Marlow impressed upon his hearers the great need for thinking as the legal mind thought. Presumably it is to collect the facts in logical sequence, and to assemble them with just sufficient gaps to leave room for an argument. In this paper the authors had purposely left gaps, to invoke argument. Mr. Jackson had seized upon some of the gaps, and had spoken about them. No one, however, had dared to say definitely whether the Americans were using the Saybolt instrument as the basis for viscosity index. It would be useful to have an authoritative statement on this one point, because then we should be in a better position to gauge their accuracy of viscosity index. The essence of this paper was to bring into bold relief that a high degree of accuracy is needed in viscosity determination when an accuracy of a few points is demanded in the calculation of viscosity index. So long as the Saybolt instrument is the preferred instrument in the U.S.A., we need not be too fussy about controlling the viscosity thermostats to plus or minus 0·025° F. Lately some embarrassment has been caused by one of the Government Departments demanding an oil with a particular viscosity index. The embarrassment lay, not in obtaining the correct viscosity index, but in deciding how many points above it it would be necessary to go to ensure meeting the specification. Clearly the answer lay exclusively in the accuracy of the viscometer which should be used. When viscosity index is translated into pence per gallon, and gallons into thousands of gallons, the importance of viscosity measurement becomes a little more obvious. The question which must be decided sooner or later is whether kinematic viscometers shall be used on all occasions when viscosity index is to be calculated. No one seems to be bold enough yet to answer that question; it is one which must be faced if we are expected to state viscosity index to an accuracy of three points. In making this statement he was not referring to the calibration of a particular instrument, or the measurement of the viscosity of a particular oil, but to oils which are being made and sold every day. We are not dealing with an academic question, but one of routine.

The Chairman then put on the blackboard the following table, showing the figures he had received from Dr. Barr, to which he had referred in his opening remarks.

	1.	2.	3.
Ubbelohde	528·7	17·77	79·00
Fenske	527·6	17·76	78·89
Absolute	528·5	17·79	79·08
U-tube (I.P. Standard Method) .	527·0	17·70	78·77

The table showed the determination made on three oils in laboratories in America, the last one being the figures determined in this country with the U-tube viscometer. He thought it would be agreed that the accuracy shown in those figures, which were determined under conditions of extreme care, were very good and supported the A.S.T.M. figure of 0·2 per cent. It was interesting to note that the figures obtained in this country were a little low, as in Table IV of the paper, where the N.P.L. figure was a little low as compared with the figure obtained by the Bureau of Standards. All three types of instruments in the I.P. Standard Methods were represented.

It appeared desirable to review the work done for the International Standards Association, and he hoped that at a later date it would be possible to present a paper summarizing all the results. The results were incomplete in the case of the Continental countries, because the samples were circulated only in May or June, 1939, and it was for this reason that no summary had yet been prepared.

Mr. R. F. Hurt said that attention had been focused mainly on the calibration of the instruments, but that it seemed to him that the oil also should be considered. Mr. Evans had referred to an oil of Viscosity Index 85, that oil being loaded with 10 per cent. of additive. What effect would that additive have on determinations of kinematic viscosities, and their reproduction by different laboratories? Discrepancies, instead of being due to apparatus, could well be inherent in the oil actually under test.

He had no doubt that all the figures given in the paper had been determined on beautifully bright, clear, moisture-free oils, but how many of the members invariably dealt with oils in that condition? A number were concerned with oils from ships' and shore tanks, or from batches in process of manufacture. Such oils would contain traces of moisture, perhaps contain an unknown additive, or have been heated in some way immediately prior to test.

The details in the I.P. handbook for the Redwood instrument provided for the question of the thermal history of the oil under consideration. It is laid down that it should be heated in a stoppered container for 1 hour at 212° F. in a suitable bath maintained at that temperature. In passing, he wondered how many laboratories, when doing ordinary Redwood viscosities for works control, followed this procedure, and how many took a sample, warmed it in a pan (which according to Redwood details is not permissible), and measured the viscosity at once.

In the older, less accurate Redwood method the advisability of a uniform heat treatment before test is recognized. This is not the case with the newer system. He felt that with regard to kinematic viscosities, there should be some ruling as to a quick preliminary thermal treatment, and so far this has not been given.

Mr. Lapitzky said that his firm had done a fair amount of calibration of viscometers, and he felt that they could obtain an accuracy to within 0·2 per cent., provided they could get a definite basic standard. That had been their main trouble. They could get a viscometer calibrated accurately provided they had an exact and reliable figure for their standard. They found that the temperature-control difficulty was not so very great, but the difficulty of obtaining suitable interconsistent standards was very considerable.

Mr. Lapitzky subsequently wrote to suggest :

(*a*) Removal of the B.S.I. viscometers, and possibly the Fenske viscometer from the I.P. Standard Methods. I know that apart from the question of accuracy many laboratories have experienced difficulties in the use of B.S.I. viscometers, and there is a feeling that these are not really suitable for petroleum work.

(*b*) The abolition of primary standards, such as water and sugar solutions, the calibration of viscometers to be effected by means of secondary oil standards only. These oil standards should be obtainable from one authority only—for example, the N.P.L.—who will guarantee their viscosity on the basis of a single master viscometer, the constant of which shall be determined from first principles. This authority might issue sub-master viscometers, calibrated against the master, to other official laboratories, who would then be in a position also to issue secondary oil standards; all these secondary oil standards then being strictly interconsistent.

(*c*) An alternative scheme would be the establishment of cetane, as suggested by Mr.

Cantor, as a primary standard, provided this material can be obtained in a sufficiently pure state and is stable in storage. The higher viscometers in the usual range would then be calibrated by a careful stepping-up process.

(*d*) In any case supplies of certified pure cetane and/or of certified secondary oil standards should be available from the I.P. The certified values allocated to these standards should definitely correlate with the oil standards supplied by the A.P.I.

Mr. H. L. West said that he would like to take the authors to task on one point. They referred in their paper to the conversion of Redwood units to kinematic units. This should not be done; convert kinematic to Redwood, but not Redwood to kinematic units. (See "Standard Methods for Testing Petroleum," Fourth Edition, 1942; Appendix, p. 383.)

He agreed with the authors that it was possible to obtain considerable variation in the calibration constants with viscosity using B.S.I. tubes. In comparing the same N.P.L. calibrated B.S.I. tube with three different Ubbelohde tubes, he had found that there was quite a large error, according to the time of flow, in the B.S.I. tube, amounting to about 0·7 per cent. with an oil of 152 centistokes, although at 351 centistokes the B.S.I. tube appeared correct. This is illustrated in the figures below.

Ubbelohde Viscometer No.	Viscosity of secondary standard oil (centistokes).	Viscosity of oil according to N.P.L. B.S.I. tube (centistokes).	Calibration constant of Ubbelohde tube.
3/20	—	152·3	0·9221
,,	—	269·7	0·9219
,,	—	351·3	0·9183
3/21	484·0	—	1·288
,,	—	152·3	1·234
,,	—	269·7	1·234
,,	—	351·3	1·229
3/22	78·99	—	1·002
,,	528·6	—	1·004
,,	484·0	—	1·001
,,	74·02	—	1·002
,,	—	152·3	1·008
,,	—	269·7	1·005
,,	—	351·3	1·001

It will be seen that the calibration constants of the Ubbelohde tubes are constant against the secondary standard oils, whereas against the oils the viscosity of which has been determined in the B.S.I. tube, the constants vary appreciably.

Since the laboratory with which he was associated had had as much experience as anyone in the use of these more or less accurate methods of determining viscosity, he would outline the procedure adopted. In the first place they used the Ubbelohde tube, and made a practice of having one or more tubes in each range carefully calibrated against secondary standard oils, using these as master tubes for calibrating other viscometers for use in the laboratory. Having satisfied themselves that the master tube was as accurate as could be obtained, the other viscometers were calibrated against the master tube, using a range of oils which were run in the master tube at the same time as in the tube being calibrated. By that means he thought they obtained fairly good calibration; also they made sure that the calibration did not vary over the range by more than $\pm 0{\cdot}1$ per cent.

With regard to the oil used for calibration, it was necessary to be quite sure that the flow of the oil was satisfactory—*i.e.*, that it is Newtonian. In commercial work he did not think it mattered so much, but for calibration purposes it was a necessity. They made sure that only highly refined oils were used when calibrating against the master tube. So far as temperature control was concerned, they controlled the thermostats used to within 0·03° F. of the temperature of the test.

He maintained that the measurement of viscosity, provided a suitable tube was used, could be carried out with quite good results. He had found that people with no experience whatever who had visited their laboratory, obtained just as good results with the apparatus as those who had been doing such work for years. So much so that he maintained that, if the control was taken out of the hands of the operator, he thought an intelligent monkey should be able to measure viscosity. The only possibility of error was that dirt or other extraneous matter would get into the tube, with the result that an incorrect time of flow would be given.

He thought it would be very useful, particularly to the smaller laboratories, if the Institute could arrange a source of secondary standard oils similar to those available from the U.S.A. through the A.P.I.

Dr. G. Barr, replying to some of the remarks made in the discussion, said it was true that the error due to inclination from the vertical was always in one direction for instruments of the Ubbelohde type, but it might be in either direction for the U-tube type.

With regard to the standardizing of the instruments, Dr. Garner had put on the blackboard a collection of four results. Could it be assumed that at any rate three of the laboratories in question had used the same standardizing oils to calibrate their viscometers? It was probable that the determinations did not in all cases profess to be absolute determinations, starting from scratch.

The Chairman thought that the Bingham viscometer was the only absolute viscometer used.

Dr. Barr asked whether the other viscometers were merely calibrated by oils supplied from outside.

The Chairman said that he thought the first two would be considered dependent on the third, but the fourth would be a combination of the first three, the American standard and the N.P.L. standard.

Dr. Barr said the point he wished to make was that uniformity of standards would obviously increase reproducibility as between one country and another. It was rather difficult, he imagined, to interchange oil samples between the United States and this country and to rely on the viscosity of that oil being constant for the requisite number of months or years.

The suggestion to use aniline as a primary substance was an interesting one, because it might overcome some of the difficulties which occurred in the stepping up from water.

With regard to stepping up from the assumed known viscosity of water to the viscosity of an oil by a series of instruments, he might mention that in the investigations to which he had referred earlier in the meeting the U-tubes which were used were not British Standard tubes, because there were none. They were merely tubes which he made up with what he thought would be suitable capillaries and which he thought would give similar times of flow, and they probably differed in a number of respects from the British Standard tubes. In that case he had managed to get concordance between the viscosity in the No. 3 range and the viscosity of water by stepping up, and he might mention that when he first discovered the discrepancy in the 40 per cent. sugar solution, he thought the simple and obvious method of getting over it would be to step up from water, as he had done before. He therefore did that, with a brand-new set of tubes, but got no confirmation at all. He did not know then at what stage in his stepping up the error had crept in, and he still did not know, because it seemed to him that, in any series in which stepping up was done, if the calibration constants could vary as they had been shown to do in some cases, the error was bound to occur. If the variations were due to drainage and similar things, surely those troubles would be liable to be just as marked in the Ubbelohde, and more marked in the Fenske than they were in the U-tube.

He would be very glad if a number of standardizing laboratories would accept one tube in the oil range as being a standard tube. The absolute viscosity corresponding with it might be subject to review occasionally. He would assume that he had a No

2½ tube which gave a time of flow of 200 seconds with a certain oil, and that other standardizing laboratories had a similar tube which would give approximately the same time of flow. Then the instruments used in different commercial laboratories could be compared directly in any country with those few standard tubes. He had always been nervous about standard oils, because he had not information as to how constant they were, but he had never had any indication that properly annealed glass tubes at any time changed their calibration constant.

Col. S. J. M. Auld wrote :—

My feeling for a long time has been that with the viscometers themselves brought to such a pitch of perfection that repeatability is consistently high, the difficulty of reproducibility must be sought elsewhere than in the simple matter of a reading of a time of flow.

While it is true that the baths are laid down to be kept at the correct temperature plus or minus 0·025° F., or a total variation of 0·05° F., I am open to doubt whether this is in practice really accomplished even in laboratories which are well fitted out. Apart from the delicacy of the thermostatic control, which itself must be good in order to achieve the accuracy demanded, I am inclined not to believe that different parts of the same bath have the same temperature. These effects translated into terms of other people's size and shape of bath, thermometers, thermostats, etc., may make thermometric measurements much more diverse than is generally considered.

Even if the difference is only a total of 0·1° C., I make out the effect can be quite marked even on an oil of only average Viscosity Index. On one of the following characteristics :

Viscosity at 210° F. . .	20·4	centistokes
" 100° F. . .	368	"
V.I.	65	

I have had some approximate calculations made. As a general rule viscosity variation per 1° C. between, say, 35° and 40° C. is from 5 to 6 per cent., according as the V.I. moves from 100 to 0. An average figure for an oil of the type suggested would be, say, 0·6 per cent. per 1° C., making a difference of 1 unit in the V.I. This difference would, of course, be increased as the viscosity decreases, and could reach a maximum of around 6. These rough calculations would appear to confirm the findings in Table I of the paper.

In connection with the diversity observed between different laboratories, I think one of our first efforts should be that of finding out what is the accuracy of the temperature measurement and control. It would look to me that the differences might easily cover quite a wide range of observed effects.

The following written communication was sent by Mr. Arthur W. Cox :—

The paper revives once more the thought that we are reaching a time when we need to consider whether the viscosity question of such heterogeneous liquids as petroleum lubricants can be dealt with adequately by one standard practice. There are two aspects of the subject.

The first is that of research. We must continue to investigate the properties of the materials with which we deal, in order to secure the most efficient and economical methods of use. The work must be of a high degree of accuracy, and requires the use of delicate apparatus under stringent conditions of control. It will be time-consuming.

The second use of viscosity measurement is the practical one of scientific control of supplies. It is dependent on the research work just referred to, but does not necessarily require the same type of apparatus or the same niceness of determination or expression. The authors of the paper appear to consider that this practical control work does not require the same conditions as research work, for, on page 3 of the preprint, when referring to I.P. Method 70/42, they say : " This precision . . . is within the requirements demanded by efficient lubrication." There are others who will agree with this statement.

If, then, it is true that a robust apparatus of simple construction used under standardized conditions can give results which enable one accurately to classify and control lubricants from the point of view of viscosity, there seems to reason no specify delicate and fragile apparatus which requires expensive and complicated controls,

in order to secure a degree of accuracy which is of no practical value. There must arise a time when we must recognize that fine differences in viscosity mean nothing from a practical point of view and that, although our methods may constantly be improved in order to obtain extreme accuracy, the value of the results may be only academic.

A further important point emerges from the paper. It appears that the accuracy of the more scientifically controlled methods may not be so great as the specifications of tolerances would indicate. If this is true there is very good reason for the suggestion of caution in use and interpretation of such results and in the plea for further investigation and consideration. The authors appear to have indicated a weakness in our proposed methods, and I suggest that the problem will be simplified if we remember that we are called upon to consider this question as part of the science of lubrication rather than the science of viscometry.

MR. J. C. CRAGG, in replying to the discussion, said that previous speakers had answered most of the points that had been raised.

The Chairman had said that the new I.P. standard method did not really say that the apparatus would measure viscosity with a maximum error of $\pm 0{\cdot}3$ per cent. but that another possible error of $\pm 0{\cdot}3$ per cent. must be expected. He thought that this ought to be made quite clear in the method of test, because anyone reading through the method was justified in thinking that any of the viscometers described would measure viscosity with an error not exceeding $\pm 0{\cdot}3$ per cent. if all the refinements of the method were observed, and the viscometers were calibrated against any of the calibration standards allowed.

He could assure Dr. Broom that he did not welcome the adoption of viscosity index as a clause in buying specifications, but, as it now seemed to have become established in some Government specifications, it was very unlikely that it could be dislodged.

With regard to the remarks made by Mr. Romney and some other speakers about probable error, he would like to point out that when the authors referred to probable error they had arrived at this quantity by assessing the maximum error and had then calculated the probable error by means of a formula. He quite appreciated the fact that most of the errors might cancel out, but some unfortunate person might make them all on the same side.

He was very interested in the remarks made by Mr. West. It had been well substantiated in the discussion, he thought, that the calibration standards were not interconsistent. It seemed to him that a high order of repeatability could be achieved if due attention was paid to the purely physical side of viscosity determination, if all the viscometers in use were calibrated against one standard only, and if the viscometers were carefully checked to ensure that their calibration constants were true constants. The general run of B.S.I. viscometers did not appear to give reliable results and very little had been said about the Fenske. The general feeling was, he thought, that suspended-level viscometers were likely to be the most reliable type. It was not possible to obtain agreement between different laboratories when all the calibration standards in question were allowed, unless the various laboratories all decided to use the same standard. A small difference in viscosity might influence the viscosity index considerably. It had been shown that a difference in viscosity of 0·7 to 1 per cent. could be obtained by the use of different calibration standards. It was fairly obvious that this state of affairs could have most unfortunate consequences.

With regard to the storage of secondary oil standards, the difference in viscosity on an oil of moderate viscosity was, he believed, about 0·2 per cent. during a year's storage under ideal conditions. A conventionally refined oil stored under similar conditions might show a variation of anything up to 1 per cent.

With regard to the liquid to use in the viscometer bath at 210° F., he could not suggest anything other than white oil, ethylene glycol, or glycerine and water.

In reply to observations that it would be better to convert kinematic viscosity to Redwood viscosity than to convert Redwood viscosity to kinematic viscosity, he would say that the idea of trying to assess the error arising from the calculation of viscosity index from measurements by the Redwood method was based on the fact that there were so many Redwood viscometers in existence. It was necessary to look at the matter from the practical point of view, but the authors were well aware that it was not a practice to be recommended.

He hoped that the various suggestions for arriving at a common calibration standard

would be pursued, as it was quite clear that until all viscosity measurements were based on one standard there would always be some element of doubt existing as to their reproducibility.

DR. A. E. DUNSTAN, in proposing a vote of thanks to the authors of the paper, said that he had been concerned with the question of the viscosity of oils for more than forty years, and was immensely interested in its development, the methods of determination and so forth, but he proposed to make his contribution to the discussion in the form of a written communication at a later date.

The vote of thanks was accorded with acclamation, and the meeting then terminated.

WARTIME CHEMICALS FROM NATURAL GAS.*

Address before American Institute of Chemists, Chemists' Club, New York. 23rd October, 1942.

By Dr. Gustav Egloff.†

For many years natural gas has been used mainly for heating and generation of steam and electrical power. In the last few years, however, the tempo of research and development has increased enormously. A much higher field of utilization for natural gas than as fuel is seen in the conversion of the hydrocarbons into superior aviation gasolines, lubricants, synthetic rubber, explosives, acetylene, anæsthetics, plant-life promoters, plastics, solvents, and many other chemical derivatives. A vast supply of these derivatives is available in natural gas produced in this country.

The processes and methods for such conversion in some instances are already in commercial use in the petroleum-refining and other industries. Other methods have been worked out in the research laboratories, and the processes and yields that can be achieved are known; but it remains necessary for further research to establish the means to reduce costs to the level of commercial practicability. Another wide avenue for future development in the natural gasoline and refining industries is thus foreseen.

Natural gas is consumed at the rate of over 2·6 trillion cu. ft. per year. The U.S.A. has proved reserves of 85 trillion cu. ft. and another 85 trillion as potential reserves. The yearly consumption of natural gas is equivalent in fuel value to 100,000,000 tons of coal or over 500,000,000 barrels of fuel oil.

In the Axis countries methane gas is a widely used substitute motor fuel. As a matter of fact, there are over 107,000 compressed-gas (methane, ethane, propane, butanes) propelled motor vehicles operating in continental Europe, which conserved about 2,300,000 barrels of gasoline for military use. The compressed gas is sold at filling stations in exactly the same way as gasoline in the U.S. The gases are compressed under pressures up to 5000 p.s.i. into steel cylinders attached to the running-board of the car or under the floor of trucks and buses. Italy has a number of natural gas-wells, and is operating many buses and trucks and a number of locomotives on methane gas. This looks like a desperate measure, since on the average about 135 lb. of steel are required for each of these high-pressure steel-alloy cylinders in order to withstand the high pressures. The products of fermentation of sewage are also used as a source of methane gas in Germany. Methane from coal gas is used for running motor vehicles of one sort or another in many of the European cities. Many coal-hydrogenation units produce gasoline in addition to methane, ethane, propane, and butanes by the Bergius and Fischer-Tropsch processes. The latter process will be re-

* Received 28th December, 1942.

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ferred to later in more detail, because it is a potential source of many products. Buses, trucks, tractors, and power shovels, numbering over 25,000 in the U.S., use compressed propane and butane. One truck company has liquefied butane functioning in a dual rôle as a refrigerant for fruits and meats, and as motor fuel for the truck after the cooling has taken place.

Hydrocarbons present in natural gas are methane, ethane, propane, butanes, pentanes, hexanes, and heptanes, etc. The first four of these are gases, while from pentane on they are liquids useful as gasoline.

The individual hydrocarbons have a variety of uses in a number of industries. Propane has been suggested for use as a fuel for breaking in aviation engines on the "testing block," since it has a high octane value and is readily available. Such a procedure would conserve the 100-octane liquid fuels needed for fighter, bomber, and cargo airplanes in the war effort. Other uses for propane which have gained wide commercial application are as refrigerants and solvents in the refining of lubricating oils. Paraffin wax, asphaltic substances, naphthenic hydrocarbons, and other materials are eliminated from lubricants when propane is used as the solvent. Over 50 per cent. of the world's lubricating oils are improved in quality by the use of propane.

Two hydrocarbons of great utility present in natural gas are *iso*butane and *iso*pentane. *iso*Butane is the key hydrocarbon in the production of aviation gasoline by alkylation with olefins. In general, there is not enough *iso*butane available, hence it has been necessary to isomerize the normal butane present in natural gas to the *iso*-compound. A number of commercial installations are in operation and under construction to isomerize normal butane to *iso*butane. Normal and *iso*pentane are also present in natural gas, and it is highly desirable to fractionate out the *iso*-compound due to its 91 octane rating in contrast to the normal, which has an octane number of 64. *iso*Pentane is blended with aviation gasoline in percentages ranging from 10 to 20, depending on the other components in the final blend.

Olefinic hydrocarbons not contained in natural gas as such, are important for many reactions, not alone for aviation gasoline, but for synthetic rubber and a host of other products. There are several methods of producing olefins from natural gas: one is by high temperature, and the other by catalysis. The olefinic hydrocarbons which are now in great demand are ethylene, propylene, butylenes, pentylenes, and butadiene. Natural gas, particularly the propane–butene fraction, when subjected to high-temperature cracking, produces ethylene, propylene, butylenes, and butadiene. Normal butane is readily converted into butadiene in one or two stages by catalytic means at high temperature, with yields reported of over 60 per cent.

A branched-chain paraffin, *iso*-octane, is of great importance in the aviation fuel programme. There are two methods whereby this hydrocarbon is derived, one is by polymerization, in which *iso*butylene is polymerized to a dimer in the presence of phosphoric acid as a catalyst. *iso*-Octene is the product, and on the addition of hydrogen, *iso*-octane results. *iso*-Octane has an octane rating of 95–100. Another method of producing aviation gasoline is to polymerize the propylene, butylenes, and pentylenes present in cracked gases to a polymer gasoline under selective conditions

which on hydrogenation yields an aviation gasoline blending product of 90 octane rating.

The polymerization process has been largely replaced by the alkylation process, in which *iso*butane is alkylated by butylenes in the presence of sulphuric or hydrofluoric acid catalysts. The resulting alkylate ranges in octane value from 91 to 96. The simplest of the olefins is ethylene, which is used to alkylate *iso*butane at temperatures in the order of 950° F. and pressures up to 5000 lb. This reaction produces neohexane having an octane rating of 94, an important hydrocarbon for aviation gasoline. In addition to alkylating ethylene and butylenes, propylene and pentylenes are also being alkylated with *iso*butane to form additional quantities of high-quality aviation gasoline. It is proposed in some type of operation to utilize the mixtures of propylene, butylenes, and pentylenes in the alkylation reaction with *iso*butane, using hydrofluoric acid as alkylating catalyst to produce alkylate of 91 octane rating, highly suitable for aviation gasoline blending stock.

An important aviation blending fuel of an entirely different type is cumene, which is produced from the alkylation of propylene and benzene in the presence of solid phosphoric acid. A number of commercial units are now in operation.

Normal hexane and heptane are two hydrocarbons which, from a motor-fuel standpoint, are practically worthless unless their molecular structure is changed. Normal heptane has a zero octane rating and hexane about 25. These straight-chain paraffin hydrocarbons, hexane and heptane, can be changed in configuration and also in their properties to improve their anti-knock properties. Hexane and heptane can also be converted into benzene and toluene—two important hydrocarbons for high explosives. Benzene is of vital importance in the production of styrene, which is produced by the alkylation of benzene with ethylene forming ethyl benzene. Dehydrogenation of this compound yields styrene. When styrene (25 per cent.) and butadiene (75 per cent.) are mixed in the presence of a catalyst such as peroxide, polymerization takes place to form the synthetic rubber Buna-S.

The synthetic rubber programme in the U.S. calls for 886,000 tons as planned in September 1942, distributed as follows:

Types.	Tons.
Buna-S	705,000
Butyl	132,000
Neoprene	49,000

However, the recommendations of the Baruch Committee called for an increase of 220,000 tons to be apportioned as:

Types.	Tons.
Buna-S	140,000
Neoprene	20,000
Thiokol	60,000

Of the total 886,000 tons of synthetic rubber planned for the U.S., 705,000 tons will come from butadiene and styrene. The normal butane that will be used for butadiene will represent about 80,000 tons a year,

largely derived from natural gas. One plant has a rated capacity of 66,000 tons, and the other 15,000 tons a year.

More than 100,000 barrels a day of normal butane are available from natural gas. If this were used just for butadiene-making, it would satisfy the entire butadiene requirements in our present synthetic rubber programme. Hence it can be seen that the natural-gas industry has more than enough of the hydrocarbons which can be converted into raw materials to supply the entire synthetic rubber programme. Another important source of butadiene is through the dehydrogenation of butylene derived from catalytic cracking. This source will yield at the rate of 283,000 tons annually.

Another type of synthetic rubber is called Thiokol, made by chlorination of ethylene, which is then refluxed with sodium polysulphide. The synthetic rubber programme calls for 60,000 tons of Thiokol yearly. Hydrogen sulphide is present in varying percentages in natural gas, and is readily converted into flowers of sulphur. This sulphur may react with caustic soda to produce sodium polysulphide. After reacting ethylene with chlorine, the dichlorethane is formed which reacts with the polysulphide, yielding Thiokol. The plans call for the use of Thiokol in re-treading of tyres.

Besides butadiene, styrene, and ethylene, a hydrocarbon of great importance is acetylene, used in the production of the synthetic rubber, neoprene; it is also the base material for nylon, a replacement product for silk. Calcium carbide is produced from coal and lime in electric furnaces requiring much electrical power. When water is added to this compound, acetylene is formed.

Natural gas, or products therefrom, under high-temperature conditions readily yield acetylene. Two commercial acetylene units are being installed at the present time, one of which will produce at the rate of 75 tons per day or 27,000 tons a year. Other units are also under way. The charging stock may be either propane, butane, natural gasoline, or fractions from petroleum. It is believed that acetylene can be produced at a lower cost from processing natural gas than by the electrochemical method of producing calcium carbide. The natural-gas industry has enormous volumes of propane and other hydrocarbons available to supply the whole needs of the United Nations for acetylene and its derivatives.

Germany uses acetylene made from calcium carbide, converting it into butadiene by a four-stage chemical process. Neoprene rubber is made from acetylene treated with hydrochloric acid. This type of rubber will be produced at the rate of 49,000 tons a year in the U.S.

The Russians start primarily with ethyl alcohol from grain to produce butadiene. Butadiene from ethyl alcohol derived from grain will be one of the sources in the U.S. synthetic rubber programme. The tonnage of butadiene from grain alcohol will be at the rate of 242,000 a year, representing about one-third of the Buna-S type production.

There are several other types of rubber which are in commercial production, one of which is the type based on *iso*butylene from dehydrogenation of *iso*butane from natural gas or from cracking of oil. *iso*Butylene is copolymerized with about 2 per cent. of butadiene or isoprene, resulting in a product called butyl rubber. In the Government programme, this

type of rubber will be produced at the rate of 132,000 tons a year. Butyl rubber, as of to-day, is not as good a synthetic rubber for tyre use as the Buna-S. Tyres made of butyl rubber have a mileage life of about 12,000 miles, with a maximum road speed of 35 miles an hour. This will naturally be improved upon.

There is an important use for synthetic rubber which is fabricated so that billions of minute air-cells are present; it is used as a liner in gasoline tanks in fighting, bombing, and pursuit planes. When a bullet goes through the tank, the rubber causes it to be self-sealing.

Another type of synthetic rubber is the acrylonitrile-butadiene which can also be produced from natural gas, and is known as Buna-N or Perbunan.

One of the necessary materials in the compounding of either natural or synthetic rubber is carbon black, which is made from natural gas. Carbon black is an important component in tyres or other rubber goods, whether it is blended with natural or synthetic rubber, as the properties of rubber, particularly from the standpoint of the tensile strength and wearing qualities under service conditions, are greatly improved. During the year 1940 about 369 billion cubic feet of natural gas were converted, largely by the channel process (air oxidation), into carbon black, with an average of 1·54 lb. per cubic foot of gas or about 285,000 tons, of which about 85 per cent. was used in tyres. Furnace black appears to be superior for use in synthetic rubber.

The world's natural-rubber production for 1941 was about 1,675,000 long tons, of which the U.S. imported over 800,000 long tons. The United Nations have lost over 95 per cent. of the world's natural-rubber sources, and Russia has lost two of its synthetic rubber plants in the Ukraine.

With the tremendously increased demand for airplanes, tanks, motor-trucks, ships, trains, gun mountings, etc., rubber is required in ever-increasing quantities by both the fighting forces and the necessary civilian users for the successful conclusion of World War II. A medium-size tank requires 500 lb. of rubber, small pontoon bridges 1000 lb., for Flying Fortresses, the gasoline tank alone requires 500 lb. of bullet-sealing rubber, while a large bomber uses 1250 lb., gas-masks 0·75 lb., and battleships between 75,000 and 150,000 lb. Tyres for large excavation trucks used by the Army have a diameter of 9·5 feet and weigh over 3500 lbs. There are many hundred more products requiring rubber that are vital in the war effort, such as blimps, barrage balloons, rubber boats, rafts, and life-saving jackets and suits for flyers, hospital rubber needs, etc. Millions of soldiers on the fighting fronts require rubber in one form or another.

The synthetic-rubber picture in the U.S., with its 886,000 tons a year at plant costs of about $800,000,000, is already well under way. The Baruch Committee has recommended that this tonnage be increased to 1,106,000 tons a year. In addition to being the arsenal for many other war products, synthetic rubber will also have to come from the United States to supply our allies' needs. It may well be assumed that even 1,106,000 tons of synthetic rubber will be too low for the United Nations' requirements.

The question arises now: Is the synthetic-rubber product equal to the natural? In general, one can say that synthetic rubber is at least equivalent to the natural; the chemist's goal is not necessarily to synthesize a duplicate of natural rubber, but it is certain that whatever properties

rubber has that are needed will not only be duplicated, but radically improved and new ones added. Synthetic rubber is superior to natural rubber in gasoline, oil, and chemical resistance. The synthetic product is more stable to light and air, and has greater wearing properties. Some trucks using synthetic-rubber tyres have gone over 35,000 miles. Side-wall tyre strength is greater, meaning greater safety and better road grip. The latter property has been tested out thoroughly on wet and muddy roads. Tests on hills with different trucks have shown that the synthetic-rubber-tyred vehicle goes up a hill with very little side-slipping, whereas the tyres of natural rubber slipped all over the road. On curves, when operating the car at high speeds, the synthetic tyre is safer than the natural.

With the number of research men in the field of synthetic rubber, with expenditure of millions of dollars yearly, one can feel confident that synthetic-rubber tyres will evolve with a life of *at least* 100,000 miles, or, expressed in another way, the tyres may well outlive the motor-car.

As far as the author is concerned, synthetic rubber in the U.S. is here to stay, and will be a permanent industry during the next peace period. With the fall of Singapore our greatest source of natural rubber was cut off. Natural rubber (December 1941) cost about 22 cents per lb. The price ranged through the years from 3·5 cents to over $1 per lb. It can be stated that synthetic rubber in mass production will cost less than 15 cents a lb.

Does this mean that natural rubber will not have its uses? As far as tyres are concerned, it will not have the dominating position it has held heretofore. One may be certain that, good as synthetic rubber is to-day, it will be far surpassed by that yet to come. The properties of the rubber desired will be under close chemical control, based on the high purity of the components started with, catalyst, and precise conditions to yield the finished product. Natural rubbers vary widely in properties, due to many factors. Producers of natural rubber depend on the life-cycle of the rubber tree, climatic and soil conditions, while the chemically produced rubber will have the exact properties for which its structure and use were designed. Natural rubber contains a number of unknown components, whereas synthetic rubber has one, two, or three components of known characteristics.

Natural gas is an important source of high explosives. In some parts of the country it is being cracked into hydrogen, which is combined with the nitrogen from the air, producing synthetic ammonia. The ammonia is readily oxidized with air into nitric acid. Combination of the ammonia and nitric acid produces ammonium nitrate.

In World War I the maximum toluene production was at the rate of 15,000,000 gallons a year, and practically all came from coal-carbonization plants to derive coke for steel-making, with toluene as a by-product. The toluene production in World War II from coal carbonization is at the rate of over 25,000,000 gallons a year. According to published reports, the demand for toluene is from 250 to 300,000,000 gallons a year—the difference between the volume of toluene from coal and the total demand will come from petroleum, *i.e.*, ten to twelve times as much from petroleum. In comparing the two wars, the demand for toluene has increased from sixteen to twenty times. On a T.N.T. basis World War I called for 150,000,000 lb., whereas the *present war calls for 3,000,000,000 lb. a year.* Benzene is readily converted into carbolic acid or phenol through chlorina-

tion and hydrolysis. Combine the phenol with nitric acid, and picric acid, a high explosive, is the result; and when synthetic ammonia reacts with picric acid, ammonium picrate, another high-grade explosive, is formed. The ammonium picrate is relatively stable, but when picric acid is used, it reacts readily with iron to form iron picrate, a very unstable compound that has a habit of exploding when least expected. That is what happened in a number of plants in World War I.

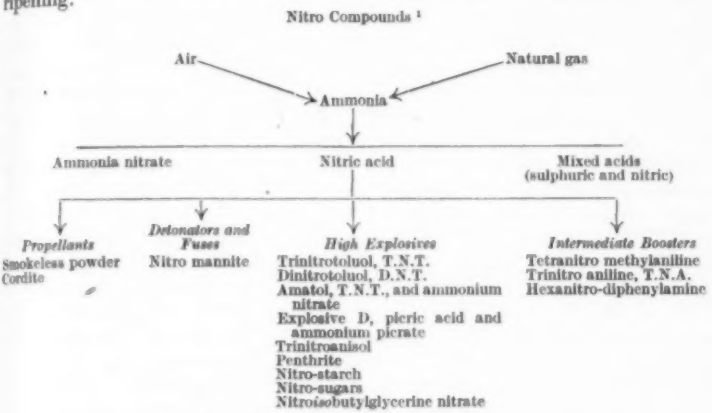
Many natural gases contain hydrogen sulphide, which, when oxidized with air, is converted into sulphuric acid, necessary in so many arts, particularly high explosives. A number of commercial units are producing sulphuric acid based on hydrogen sulphide or elemental sulphur produced from natural gas as a starting material. So we have sulphuric and nitric acid, both produced from natural gases, raw materials necessary for high explosives needed in this present war, some of which are on a scale over twenty times that of World War I.

An important substance in war is glycerine for the production of trinitroglycerine, the commonest form of which is dynamite. The main source of glycerine has been in the splitting of fats to glycerine and fatty acids in the soap-making industry. As is well known, a campaign has been launched by our Government for the conservation of cooking fats of all kinds. These fats have many uses, one of them being the manufacture of soap and glycerine. A few years ago a glycerine-making process was developed by the petroleum industry, starting with propane or propylene, which are chlorinated and then hydrolyzed to glycerine. The glycerine is then nitrated to trinitroglycerine.

Nitroparaffins from natural gas may well develop into one of the newer and valuable sources of high explosives. Methane gas, when nitrated, produces tetranitromethane. This compound is the most destructive explosive known to man. This product is a very high explosive, extremely difficult to handle. About twenty years ago in a university laboratory in Switzerland, they were working with tetranitromethane which is usually a reaction product of toluene nitration in small concentrations. *Ten grams of tetranitromethane* killed ten individuals, wounded twenty, and nearly wrecked the building. Unfortunately, no commercial process has been worked out to make this product available for use by our armed forces. Fig. 1 shows the importance of nitro-compounds in the manufacture of explosives.

Anæsthetics are vital in a world at war. One of the primary needs of the medical profession has been anæsthetics which have no post-operative dangers due to pneumonia and nausea. Ethylene has been shown to have properties superior to those of ether and nitrous oxide. Deep surgical anæsthesia is readily induced by ethylene, and insensibility to pain comes rather quickly. A general feeling of well-being and comfort, with no harmful after-effects, is present when ethylene is used. *cyclo*Propane, although known since the year 1882, was still a laboratory curiosity until the end of 1930, when it was first applied in human anæsthesia. It has since been rather widely adopted as being one of the safest anæsthetics. *cyclo*Propane, produced from either propane or propylene by a series of chemical reactions, is less explosive in the hospital than either ether or ethylene.

Olefins have been investigated as fruit-ripening agents and for use in inducing an accelerated plant-growth. The first gas to be utilised for this purpose was ethylene, which was first used in an impure form—the fumes from a kerosine stove were found to be effective in bringing about the ripening of citrus fruits. Ethylene was the agent responsible for the ripening.



[1] F. H. Dotterweich, *Refiner*, 1942, **21**, 53, 51–6.

FIG. 1.

Ethylene and propylene stimulate potato growth, and have been found to shorten the growth season for tomatoes, grapefruit, and oranges. The German Botanical Society reports that up to a 100 per cent. increase in the yield of potatoes can be obtained when the seeds are treated with ethylene gas. "The tubers of plants grown from seed potatoes which had been exposed for 24 hours to atmospheres containing 7·5, 15, or 30 per cent. gas at 65° F. were more numerous, larger, and richer in vitamin C. It is claimed that this process is cheaper than the application of hormones."

Researches by the Russians on butylene gas showed a stimulating effect on the maturing time of such trees as the walnut, peach, apple, cherry, plum, apricot, and pear. In periods when the season is too short to allow the full maturing, due to winter weather being so prolonged that flower-formation and fruit-setting are delayed, butylene may be used to hasten the growth period. The procedure adapted to plant treatment consists of enclosing the trees in tents or gas-tight covers for about two weeks before the normal or desired leafing—*i.e.*, start of the growth cycle. Butylene is passed into the tent in about 1 part per 100,000 parts of air, at temperatures between 69° and 100° F. for a period of 1–2 hours.

Another method for ripening fruits is to use pentylenes, hexylenes, and heptylenes from cracked gasoline. Addition products of the unsaturated hydrocarbons derived from cracking, such as ethylene di-iodide, ethylene butyrohydrin, ethylene acetohydrin, and ethylene formohydrin, are also used as agents for furthering the ripening of fruit.

The skin of the green fruit absorbs the olefin or olefin derivative, destroy-

ing the chlorophyll. The advantage in using liquids as ripening agents is that they are absorbed and continue their action after removing the fruit from the liquid; after storage under normal conditions, the ripening is complete.

Natural-gas hydrocarbons can be used as basic materials for the synthesis of plastics after forming olefinic hydrocarbons. There are three basic reactions which in various combinations are used to produce plastics from the derived hydrocarbons; they are oxidation, halogenation (mostly chlorine is used), and polymerization. Stemming from these reactions, the entire plastics industry has built up new materials and replacement products for many structural materials and rubber. Fig. 2 shows some of the derivatives of the unsaturated hydrocarbons from natural gas.[1]

The materials which are outlined in the chart have many uses besides plastics, as the intermediates shown are a typical cross-section of the chemicals derived from natural gas. The finished plastics, as well as the intermediate compounds, find use as paints, varnishes, addition products for lubricating oils, and moulded materials. Their intermediates are used as solvents, cleaning agents, and as additives for various types of products.

The coming importance of plastics cannot be over-emphasized at this time, since airplane manufacturing is calling for more of the plastics for use in plywood planes. Steel now used in many places is being replaced by plastics. In the war industries, where the fabrication of planes takes place, the methylmethacrylate resins are used as the transparent, non-shatterable parts where great visibility is necessary, and this will undoubtedly be used by the automobile industry after the war. A high degree of visibility from all over the motor-car will be worked into the new design, requiring less supporting framework, and a clear-vision rooftop with sliding window will undoubtedly take the place of present designs. In fact, the motor-car of the future may well be substantially all plastics.

At the present time any of the components necessary for the manufacture of plastics of all types can be made from natural gas. One of the important substances for the Bakelite type of plastic manufacture is formaldehyde, made largely from the methanol or wood alcohol by the catalytic reaction of carbon monoxide and hydrogen at high pressures. For a number of years formaldehyde and methanol have been produced from the oxidation by air of natural gas. This process can be readily expanded to produce all the formaldehyde necessary in the ever-expanding Bakelite programme. The phenol or carbolic acid and cresols, etc., are also potentially available from natural gasoline.

One big field of research and development that merits discussion is carbon monoxide and hydrogen, or the water-gas reaction to form hydrocarbons. In the U.S. we have over 2·6 trillion cubic feet of natural gas yearly production. This gas contains about 80 per cent. of methane, which can be converted into carbon monoxide and hydrogen by high temperatures in the presence of steam. In Germany the Fischer-Tropsch process has been developed to produce oil from carbon monoxide and hydrogen at the rate of about 15,000,000 barrels a year. The hydrocarbons produced are methane, ethane, ethylene, propane, propylene, butanes, butylenes,

[1] R. L. Wakeman, *Nat. Petrol. News*, 23rd July, 1941, p. R-226.

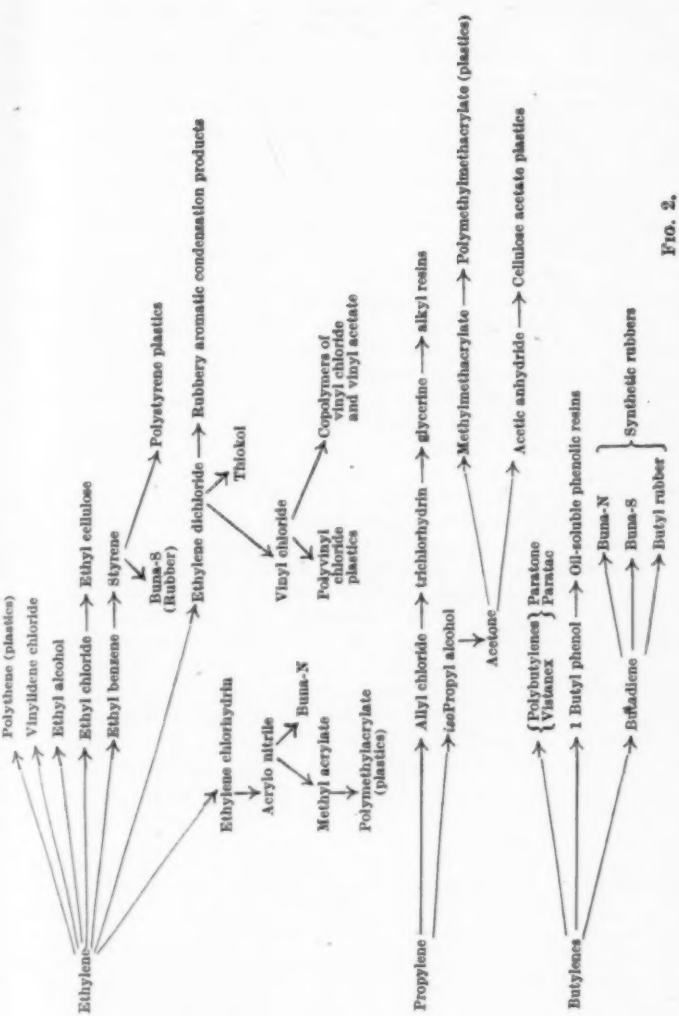

Polythene (plastics)
Vinylidene chloride
Ethyl alcohol
Ethyl chloride
Ethyl benzene
Ethylene
Ethyl cellulose
Styrene
Buna-S (Rubber)
Polystyrene plastics
Ethylene dichloride
Rubbery aromatic condensation products
Thiokol
Ethylene chlorhydrin
Acrylo nitrile
Buna-N
Methyl acrylate
Polymethylacrylate (plastics)
Vinyl chloride
Copolymers of vinyl chloride and vinyl acetate
Polyvinyl chloride plastics
Propylene
Allyl chloride
trichlorhydrin
glycerine
alkyl resins
isoPropyl alcohol
Acetone
Methylmethacrylate
Polymethylmethacrylate (plastics)
Acetic anhydride
Cellulose acetate plastics
{Polybutylenes Paratone
{Vistanex Paratac
Butylenes
1 Butyl phenol
Oil-soluble phenolic resins
Butadiene
Buna-N
Buna-S
Synthetic rubbers
Butyl rubber

FIG. 2.

gasoline, gas oil, and diesel oil to solid paraffin wax. The reaction takes place in the presence of a catalyst, which may be oxides of nickel, chromium, or cobalt, using temperatures of 400° F. and pressures of the order of 200 lb.

The gasoline produced by the water-gas reaction is poor in quality with about a 40-octane rating. The gasoline has to be cracked thermally or catalytically into higher-octane fuel. The gasoline fraction boiling up to 300° F. contains olefins which polymerize with each other to form lubricating oil. These lubricating oils are produced commercially in Germany, and some of them are high grade. The balance of the gasoline fraction—the paraffins, hexanes, heptanes, octanes—may be thermally cracked under controlled conditions to make more olefins, which in turn are converted into lubricating oil by polymerization. A portion of the synthetic oil is a high-grade diesel oil with octane number of over 100. The diesel-oil fraction is blended with lower-grade diesel oils to improve its quality.

Paraffin wax, which is also derived from the water-gas reaction, is oxidized with air to make fatty acids. The fatty acids are reacted with potassium or sodium hydroxide, and soap is produced. The last report out of Germany is that one small cake of soap is alloted per inhabitant per month, and much of it comes from this paraffin wax. In 1938, and previous years also, conversion of paraffin wax from the water-gas reaction, coal carbonization, and petroleum, was carried out, forming fatty acids. In addition, these fatty acids are combined with synthetic glycerine to make *fats for food*. Glycerine and soap are produced (U.S.) from the splitting of fats, but the Germans are reversing the process in order to produce edible fats for food. It is not the type of fats to which we are accustomed, but it is helpful under the critical food conditions existing in Europe.

An enormous amount of research is going forward in a study of natural gas and gasoline to enhance their importance in the war effort—through solvents, plastics, high explosives, acetylene, synthetic rubber, lubricating oils, and aviation gasoline. As a matter of fact, if one starts with methane gas alone, all the known synthetic products that man has produced in organic chemistry can be derived, and there are over 500,000 different ones. *Any synthetic product desired can be produced at a price*; the hydrocarbons are all potentially available to be converted into the manifold products that man requires in a modern world.